Electrical and Optical Properties of Electrochromic Devices Utilizing Solid Polymer Electrolytes

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Abstract

We describe the preparation, electrical and optical analysis of prototype electrochromic electrodes and solid polymer electrolyes and complete switching devices. The electrodes studied are nickel oxide, nickel-manganese oxide, nickel-cobalt oxide, and tungsten-molybdenum oxide. These electrodes were found to be useful as active electrochromics or ion storage layers. Solid polymer electrolytes were synthesized from poly(ethylene oxide), a-PEO, and poly(ethyleneimine). Also, an inorganic borate silicate glass was used as an ion conductor. The best performing devices were made with a-PEO electrolytes. Electrochromic devices were made using nickel oxide/tungsten-molybdenum, and nickel oxide/nickel-manganese electrode combinations. Optical spectra as a function of voltage was obtained for each device. Our best nickel oxide/a-PEO/tungsten-molybdenum device showed the photopic transmittance (T_p) to be T_p(bleached)=0.79 and T_p(colored)=0.39. The corresponding integrated solar transmittance was (T_s) to be T_s(bleached)=0.55, T_s(colored)=0.35 . Our best nickel oxide/nickel-manganese device showed the photopic transmittance to be T_p(bleached)=0.71and T_p(colored)=0.23. The corresponding integrated solar transmittance was T_s(bleached)=0.52, T_s(colored)=0.44 . Better device properties are expected with improvements in the solid polymer electrolyte.

Introduction

A number of electrochromic switching materials have been studied in the past few years [1]. For windows and other large-scale applications, the most promising materials appear to be tungsten oxide, nickel oxide, vanadium oxid eand polyaniline [2,3]. Recently, there has been an increase in the interest in electrochromic nickel oxide for electrochromic switchable windows among other applications. One of the great challenges is to develop an all-solid-state device using nickel oxide. A further goal is to develop a two electrochromic complementary device, such as nickel oxide and tungsten oxide. The work detailed here is in pursuant of these goals. In the sections to follow, several electrochromic electrodes, specifically nickel oxide and tungsten-molybdenum oxide have been developed as active electrodes. For ion storage electrodes nickel manganese oxide and nickel-cobalt oxide electrodes have been investigated. For the construction of devices we have also developed polymer ion conductors to serve as a transport media and as an adhesive lamination media. In this study we will report on our experiments with amorphous polyoxides and other materials.

In prior work, we have studied the switching characteristics and the optical properties of nickel oxide in liquid electrolytes [4,5]. In other studies we have analyzed the chemistry of these films by in-situ spectroscopic studies [6] and investigated their stability and durability [7]. We studied the properties of devices made with polymeric quarternary ammonium hydroxide, which switched nickel oxide well but had disadvantages of etching nickel oxide and outgassing [8].

With successful demonstration of switchable nickel oxide films in a liquid electrolyte, we have turned our attention toward more practical device designs based on nickel oxide. Because liquid electrolytes are impractical for large-scale devices because of sealing and hydrostatic pressure problems we have studied the alternative solid-state electrolytes. We have developed amorphous polyethylene oxide and related co-polymers such as amorphous oxmethylene poly(oxethylene) and other polymers such as poly(ethyleneimine) have been used as matrix polymers. These polymers are ionic conductors in their amorphous condition. To enhance hydroxyl conductivity of these polymers various metal oxides have been added to them.

The electrochromic device consists of fivelayers: (1) transparent electronic conductor on glass, (2) electrochromic nickel oxide, (3) polymer electrolyte, (4) ion storage layer, and (5) transparent

electronic conductor on glass. The device will color or bleach when a potential difference of a few volts is applied between the working electrode and the counter-electrode. In the experiments described below we developed nickel oxide film as active electrodes, nickel-manganese oxide and nickel-cobalt oxide electrodes for ion storage electrodes, tungsten-molybdenum oxide electrodes for complementary electrodes, polymer electrolytes based on polyoxides, and polymer laminated devices. These materials are described by their current-voltage response, voltammetry, and optical properties.

General Experimental Procedures

Nickel oxide films were anodically deposited onto a conductive fluorine-doped, tin oxide-coated glass, using the same technique described in our previous studies [3,5,6]. A Princeton Applied Research, Models 173 and 362 Scanning Potentiostats and BAS model CV-27 potentiostat with columbmeter were used to anodically deposit the coatings. All films were deposited potentiostatically onto conductive indium-tin-oxide (ITO) coated electrodes (Donnelly Co, Holland, MI) from an appropriate deposition solution. The ITO electrodes were ultrasonically cleaned, dipped in ethyl alcohol and dipped in 10-20% sulfuric acid, rinsed in distilled water and dried in nitrogen. In all electrode experiments the reference electrode was a Standard Calomel Electrode (SCE).In in-situ spectrophotometry a special quartz microcell was used with a micro-calomel reference electrode. The counter electrode was a platinum sheet electrode. Integrated charge during cycling was monitored using a strip chart recorder. Both current and voltage were monitored during deposition and cycling by a H-P/Moseley Model 7005B X-Y recorder . After electrode deposition all electrodes were rinsed in distilled water and dried with nitrogen. Most electrodes were 3 x 5 cm and in size. The active area as electrodes was 12.6 cm^2. For devices the active area was 3 x 3 cm or 9 cm^2. Some samples were 2 x 4 cm, with active area of 6.4 cm^2.

Optical transmittance measurements were performed using a computer controlled Perkin-Elmer Lambda 7 and Cary 14 Spectrophotometers For liquid device measurements a special quartz cell (2 x 10 x 7 cm) was fabricated and a micro-calomel reference electrode was added. The path length was 2 cm. The counter-electrode was platinum.

Results and Discussion

1. Nickel oxide electrodes

Nickel oxide films were deposited from a solution of 0.1M $NiSO_4 \cdot 6H_2O$ and 0.1M NH_4OH. The applied potential was a triangle potential from -200 mV to +1200 mV (SCE), with potential sweep rate of 50 mV/s. The voltammetry of the deposition process is shown in Fig. 1 for a nickel oxide electrode. Here 32 scans are shown. Typically to deposit 120 nm of nickel oxide 10 scans are needed. Fig. 2 shows the difference in optical properties for electrodes made with 8 (100 nm) and 32 (200 nm) scans. Even thicker films of nickel oxide can give peak transmittance changes as high as 70%. During deposition, the characteristic coloring and bleaching are noted. During successive deposition there is a shift in the coloration peak from 950 mV to 1050 mV, while the bleaching peak broadens and moves from 450 mV to 250 mV. The charge capacity of each cycle is greater than that of each successive cycle.

The voltammetry of the electrodes was analyzed using a sawtooth potential ranging from -400 to 900 mV at a scan rate of 50 mV/s. While the voltammetry curves are monitored, it was possible to observe the switching of the device from the bleached (transparent), to the colored (brown bronze) state. After the first few cycles the I/V voltammetry curves tend to exhibit reproducible behavior. The reduction peak is quite distinct from that of the hydrogen gas evolution peak. Exceeding the potential for the hydrogen evolution peak causes the nickel oxide layer to etch. The oxygen gas

evolution peak is close to the anodic oxidation peak and has been observed by other investigators [9-11]. We cycled the electrodes in LiOH to increase the oxygen overvoltage, compared to KOH [8,12,13].

The addition of lithium ions alters the chemical binding and electrostatic forces in the layered lattice of nickel hydroxide and increases the oxygen overvoltage by hindering the recombination of adsorbed oxygen.[14] The lithium ions help to tightly bind water in the interlayer structure of nickel hydroxide.[15] These factors provide the nickel hydroxide electrode with greater charge capacity. This effect and the voltammetry are discussed elsewhere [8].
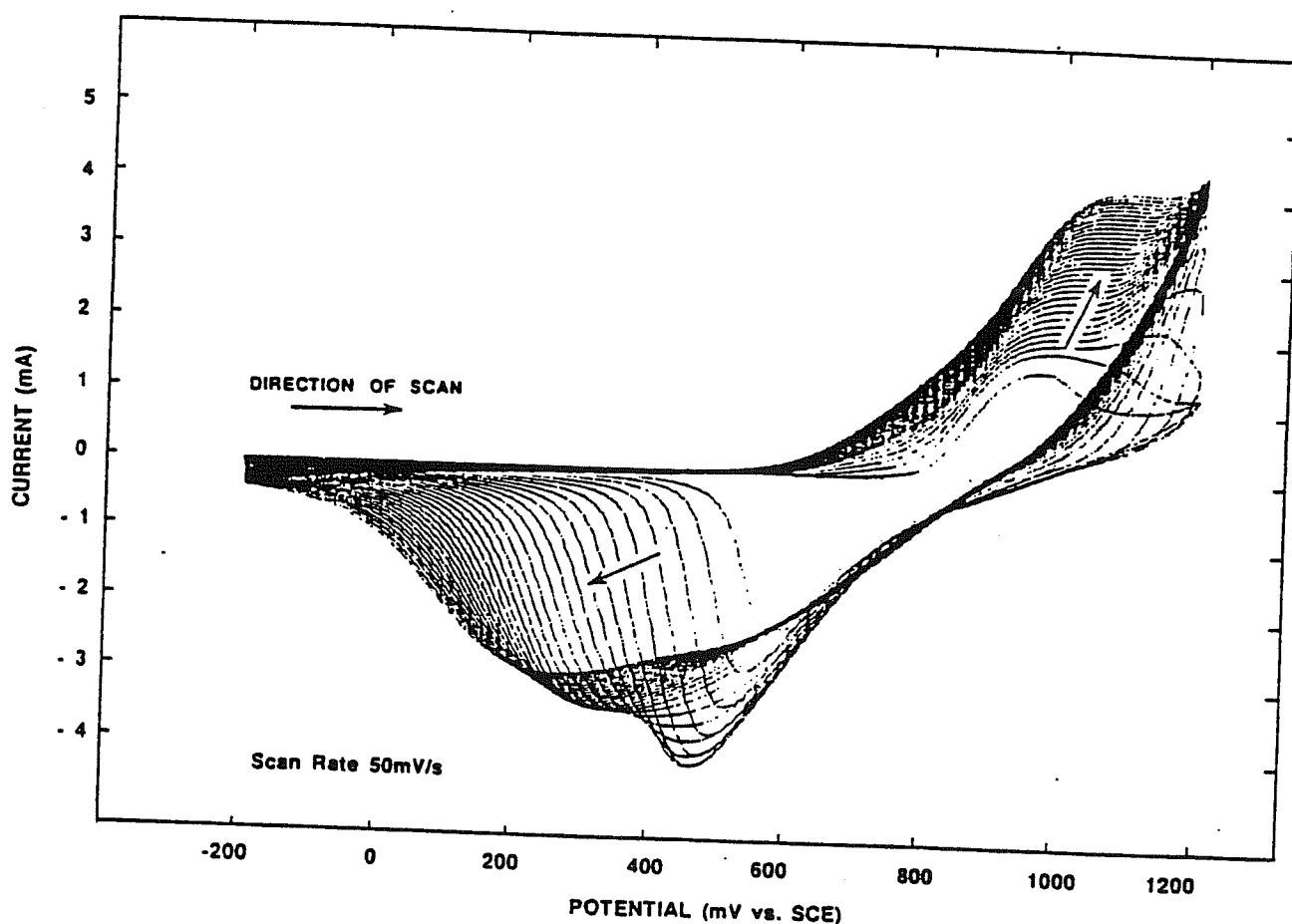
Fig. 1. Voltammetry of the electrochromic nickel oxide deposition process from a sulfate solution; 32 scans are shown. The active electrode area is 12.6 cm^2.
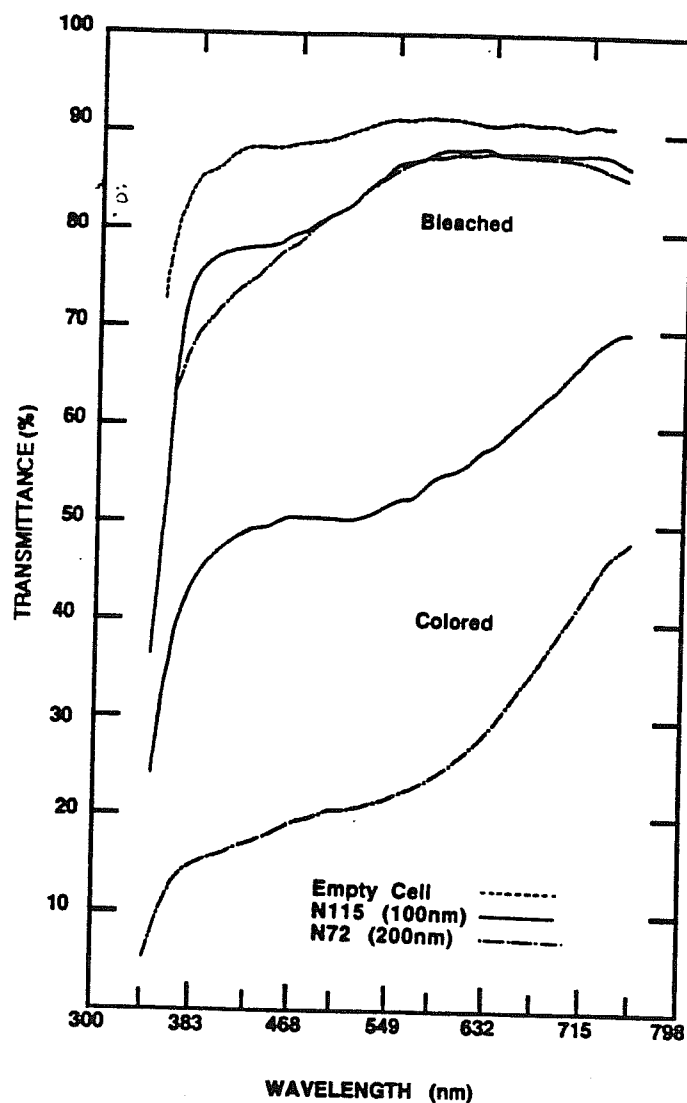
Fig. 2. Transmittance change for two different thicknesses of nickel oxide, 100 nm (8 deposition cycles), and 200 nm (32 deposition cycles). The highest curve is the empty cell response.

The charge-discharge relationship is shown in Fig. 3 for an applied triangle potential. Here we see the typical current surge upon coloration (around 60 s), showing the coloration peak followed by part of the oxygen evolution peak. Normally the voltage would be controlled to restrict the generation of the oxygen evolution peak. Also the impedence of the electrode is falling with higher potential, which will act to increase current. The discharge side of the coloration peak shows a fast discharge response. The bleaching peak also has two characteristics, first a slow negative charging to -2 mA, followed by a faster charging peak (at about 90 s) and a fast discharge to 0 mA. The last few mC discharge slowly. These current characteristics are very important for device stability.
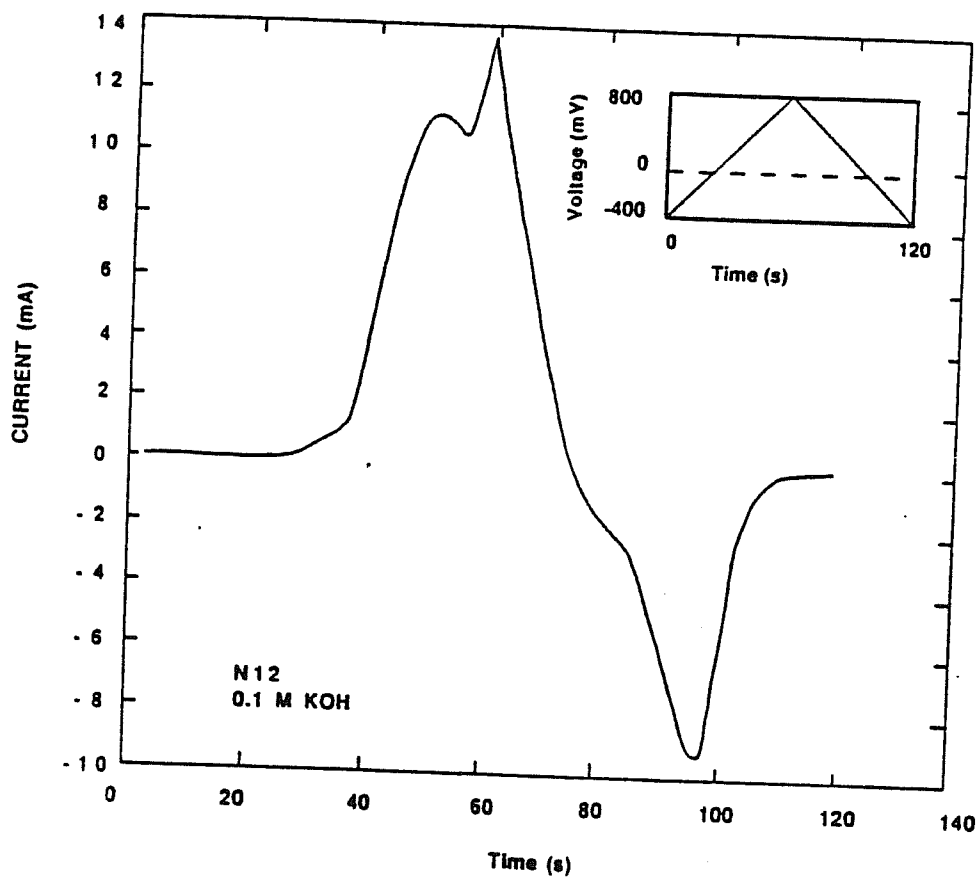
Fig. 3. Charge-discharge relationship for a nickel oxide electrode in 0.1 M LiOH. The applied potential was a d.c triangle potential, shown in inset. The scan rate is 20 mV/s. The active electrode area is 4 cm².

Normal transmittance measurements on the switching devices were performed over the visible and near-infrared wavelength regions. The electrode was colored using static potentials ranging from 0 to 0.6V with current controlled below 100 mA. The electrolyte was 0.1M LiOH. The typical spectral transmittance (250-1100 nm) of a nickel oxide electrode in a microcell is reported in Fig. 4. Also, shown in this figure is the transmittance of the empty cell, which only contains the LiOH electrolyte. The switching from 1100 to 2500 nm is less than 10% (not shown in the figure). The Spectral Coloration Efficiency is shown in Fig. 5.
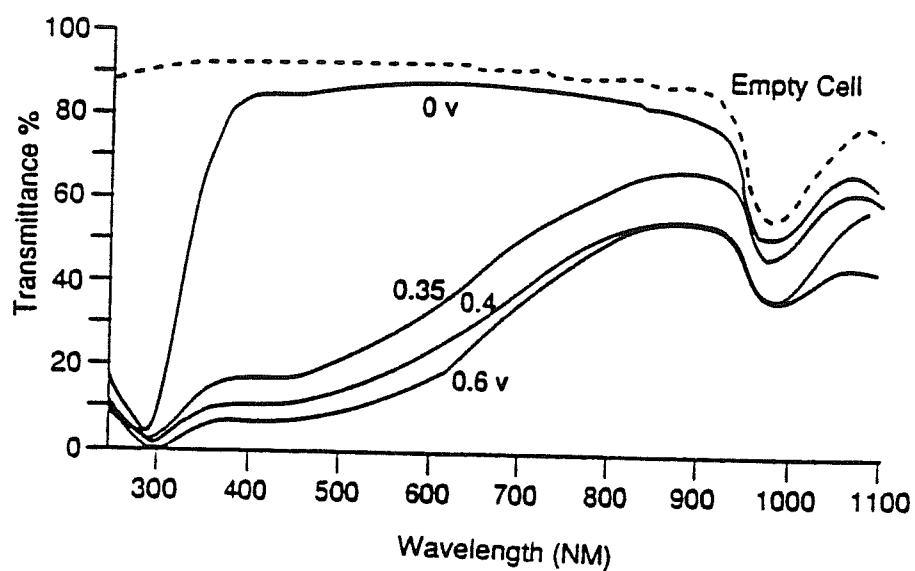
Fig. 4. Normal transmittance for electrochromic nickel oxide in a liquid microcell with 0.1M LiOH electrolyte. Transmittance is shown for different voltages (V vs SCE).
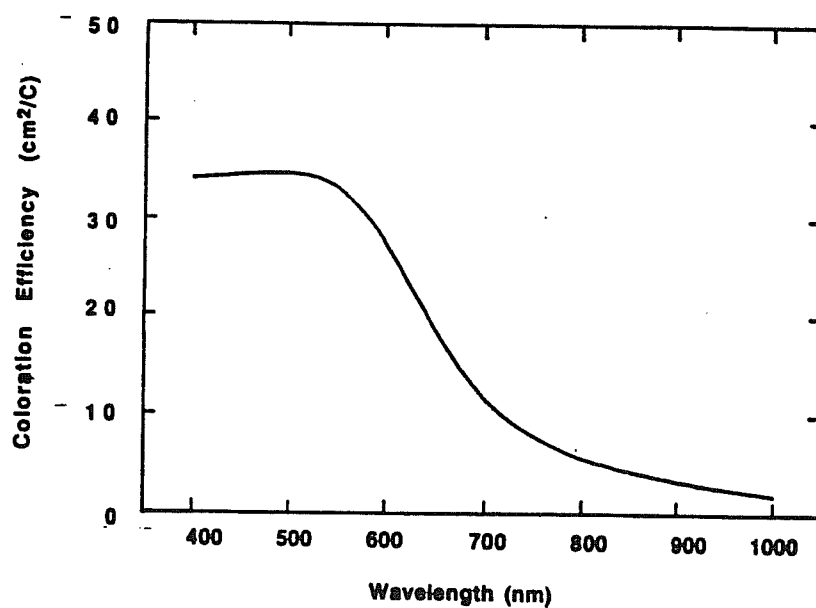

Fig. 5. Spectral Coloration Efficiency for a nickel oxide electrode in 0.1 M LiOH.

2. Nickel-manganese oxide electrodes

Nickel-manganese oxide films were investigated to serve as active electrochromic electrodes with high switching coloration or as ion storage electrodes with high transparency but low coloration. As ion storage electrodes, this material would be useful as the counter-electrode for a nickel oxide device. As active electrodes this material could be used in place of nickel oxide. For active electrodes it has been shown that the incorporation of manganese increases the coloration efficiency and stability of nickel oxide, deposited from nitrate solutions [16]. It is presumed that incorporated ions may alter the expansion/contraction of the nickel oxide lattice during cycling, increasing its stability [17].

Nickel-manganese oxide films were deposited onto ITO electrodes from a solution of 0.1M $NiSO_4 \cdot 6H_2O$ and 0.1M $MnSO_4 \cdot 6H_2O$ and 0.1M NH_4OH. We found that stable nickel-manganese oxide films could be made from sulfate solutions. A range of 1-100% manganese sulfate to nickel sulfate concentrations were used to deposit films. Throughout this work the percentages refer to solution bath concentration relative to nickel sulfate, they do not refer to the chemical composition of the film. Although, one film (30% Ni and 70% Mn) was analyzed by XPS and found to have film composition ratio the as the deposition concentration ratio. The ratio of sulfate to ammonium ion concentration was kept constant. The applied potential for deposition was a triangle potential from -400 mV to +900 mV (SCE) with sweep rate of 50 mV/s.

For voltammetry, and optical transmittance measurements, the electrodes were cycled in 0.1M LiOH for voltammetry using a calomel electrode and platinum counter-electrode. A voltage range of -400 to 900 mV at a scan rate of 50 mV was used. Cyclic voltammetry for several nickel-manganese electrodes is shown in Figs. 6 and 7. In Fig. 6, a manganese coloration peak begins to form at 4% manganese concentration at 350 mV and shifts to lower potentials at higher concentrations. The bleaching peak shifts from 250 mV to 150 mV. In Fig.7, at 20% concentration one broad coloration peak is noted at 625 mV. The addition of manganese beneficially increased the oxygen overvoltage. From 20-50% manganese concentrations the charge capacity of the electrode is good. The 80% manganese oxide electrode is stable but the charge capacity of the electrode is low. Pure manganese oxide films were found to be unstable, during cycling. Further information on manganese oxide can be found in our prior work[18].

The optical transmittance of nickel oxide and nickel-manganese oxide electrodes are shown in Figs. 8-10. Both the bleached and colored conditions are shown, data for each electrode is given in Table1. In Fig. 8. the broad optical absorption peak for nickel oxide (sample N115) is noted at 550 nm with a transmittance change of about 35%. For the nickel-manganese electrode (4% manganese solution concentration), the range of optical switching has increased slightly. The shape of the absorption curve signifys a change in color compared to nickel. The nickel-manganese films are golden-yellow in color. In Fig. 9 At 20% and 40% manganese concentration, the optical switching range is even lower, as shown in Fig. 9. The peak absorption wavelength has shifted to lower wavelengths, but the bleached transmittance is still high. Above 80% concentration, the transmittance change is less than 15 % (see Fig. 10.).

Our results show that mixed manganese-nickel electrodes have good transparency, all appear yellow or yellow brown as deposited. They are all about $T_p=0.8$ in the bleached state, but their range of switching is less compared to nickel oxide. For concentrations up to 40%, the switching is fairly good and the voltammetry is good. The upward shift in oxygen overvoltage is beneficial to the stability of nickel oxide electrodes. As a storage electrode, the concentration from 50-80% appears to be useful, if increased effective charge capacity can be obtained by increased film thickness.

Table 1. Nickel Oxide and Nickel-Manganese Oxide Electrodes

Electrode	Peak λ,nm	ΔT_{peak}	ΔT_{550}	T_p(B-C)	T_s(B-C)
N115	550	34.7	34.7	85-50	
NM118(4%)	545	36.5	36.4	83-44	55-40
NM111(20%)	440	42.5	36	80-41	
NM112(40%)	420	36	29.2	74-44	
NM113(60%)	390	26	19.2	80-60	54-47
NM114(80%)	380	15	9.2	80-75	
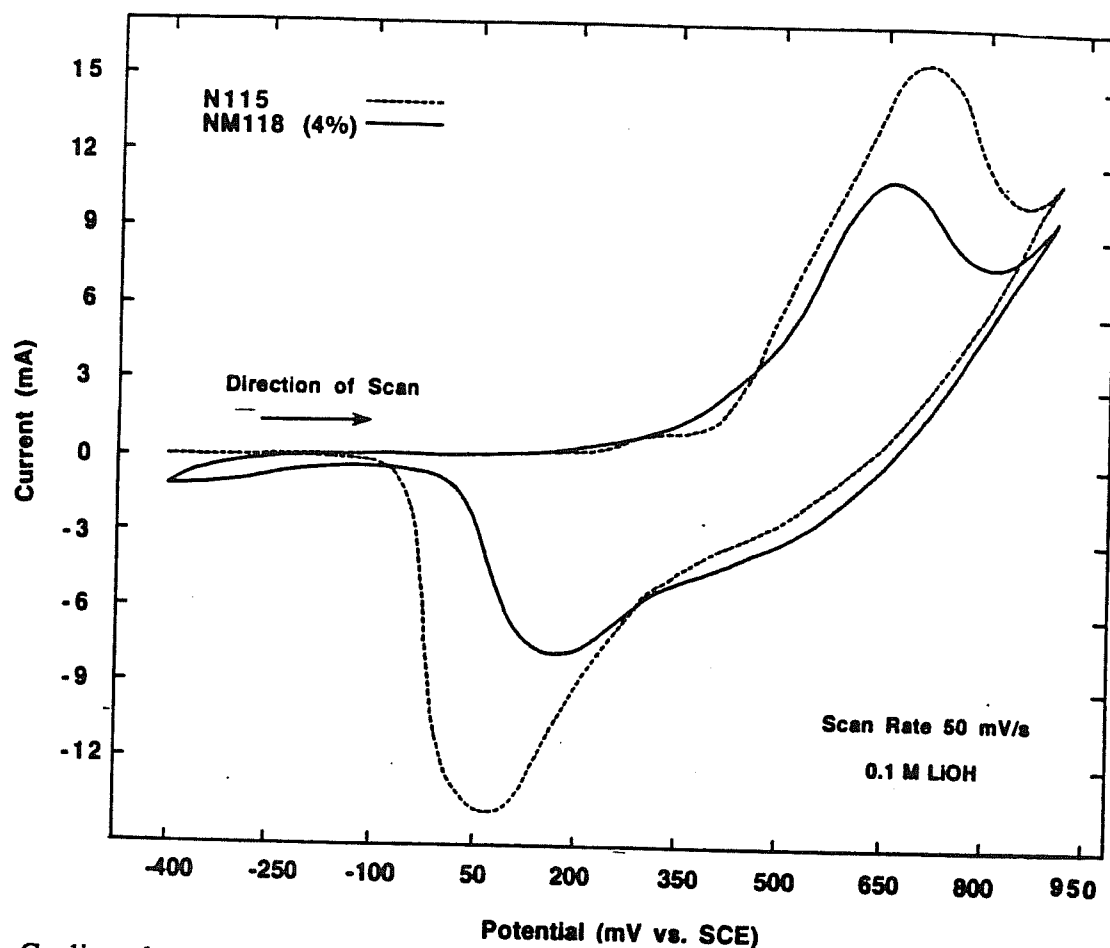
Fig. 6. Cyclic voltammetry of electrochromic nickel-manganese oxide, cycled in 0.1 M LiOH at 50 mV/s.
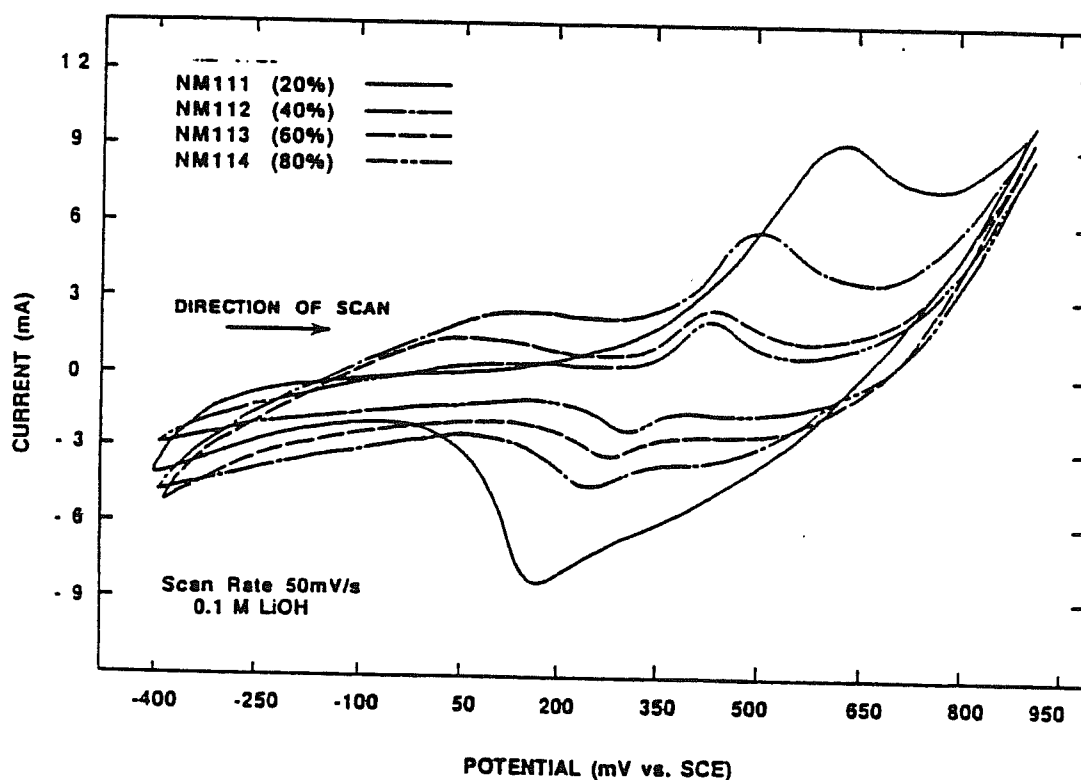
Fig. 7. Voltammetry of electrochromic nickel-manganese oxide electrodes. They are cycled in 0.1 M LiOH at 50 mV.
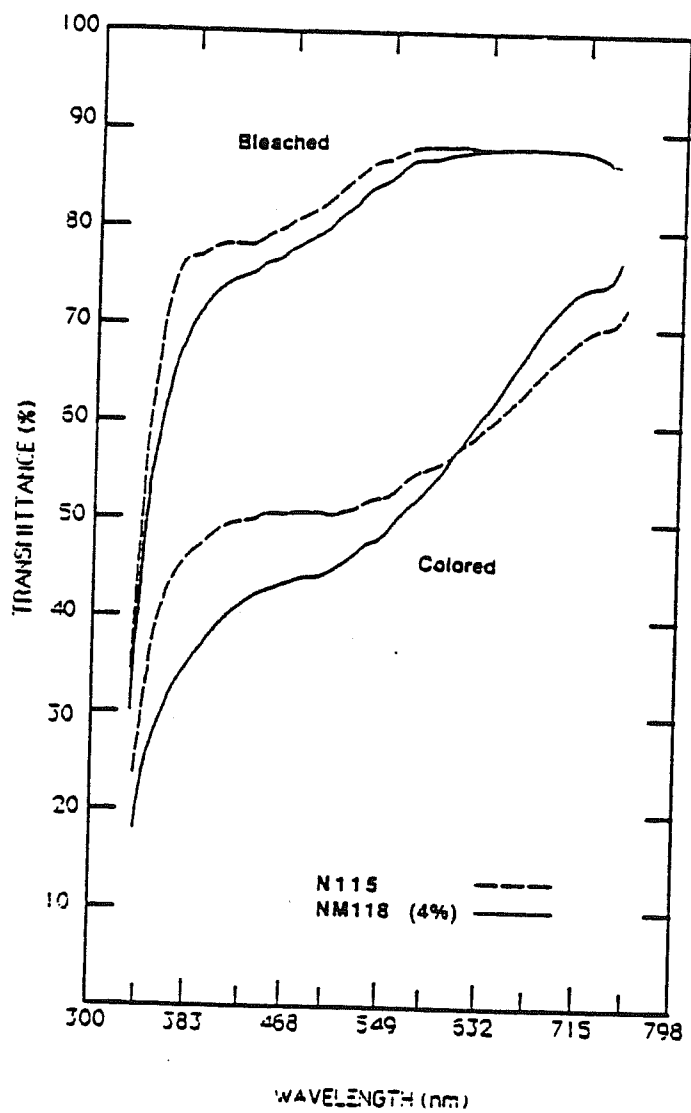
Fig.8. Optical transmittance of electrochromic nickel oxide and nickel-manganese oxide on ITO Glass. Low manganese concentrations are shown.
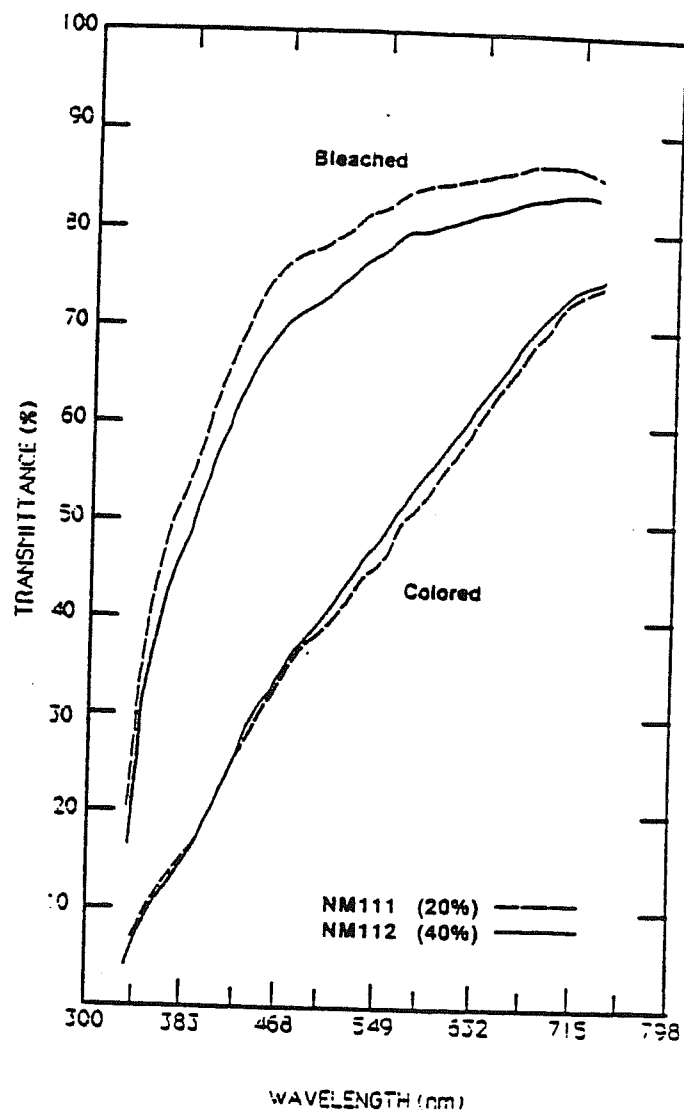
Fig. 9. Optical transmittance of electro-chromic nickel-manganese oxide on ITO glass. High Manganese concentrations are shown.
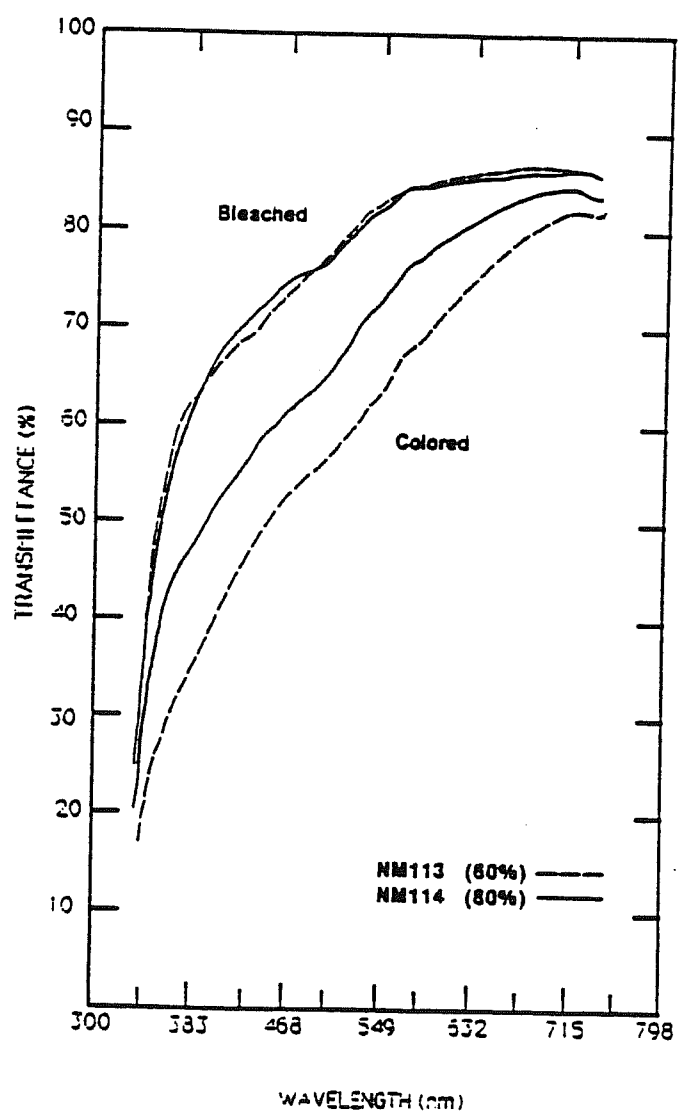
Fig. 10. Optical transmittance of electrochromic nickel-manganese oxide electrodes. High manganese concentrations are shown.

3. Nickel-cobalt oxide electrodes

Nickel-cobalt oxide films were fabricated to determine the effect of cobalt on the electrochromic response of nickel oxide. It has been shown that cobalt additions to nickel oxide can increase stability and electrode utilization efficiency [18]. The current understanding of the effect on the structure of nickel oxide is that the cobalt ions occupy both the substitutional nickel sites and interlamellar sites. This was determined by Extended X-ray Absorption Fine Structure (EXAFS) studies [19]. Also, the work was done to see if the cobalt-nickel oxide system will yield a non-coloring, nickel oxide compatible ion storage electrode. Cobalt oxide and nickel oxide are very similar electrochemically [20].

Nickel-cobalt oxide films were deposited onto ITO electrodes from solutions of 0.1M $NiSO_4 \cdot 6H_2O$ and 0.1M $CoSO_4 \cdot 6H_2O$ and 0.1M NH_4OH. A range of 1 to 100% cobalt sulfate to nickel sulfate concentrations were used. The ratio of sulfate to ammonium ion concentration was kept constant. The applied potential for deposition was a triangle potential from -200 mV to +1100 mV (SCE), with sweep rate of 50 mV/s.

For voltammetry, and optical transmittance measurements, the electrodes were cycled in 0.1m LiOH for voltammetry using a calomel electrode and platinum counter-electrode. A voltage range of -400 to 800 mV at a scan rate of 50 mV was used. Cyclic voltammetry for a range of cobalt-nickel electrodes is shown in Figs. 11, and 12. In Fig. 11, a cobalt coloration peak begins to form at 4% concentration at 350 mV and shifts to lower potentials at higher concentrations. The bleaching peak shifts from 250 mV to 150 mV. In Fig. 12, at 20% two broad peaks are noted in the coloration at 200 and 600 mV, so the addition of cobalt has increased the oxygen evolution potential. Above 20% cobalt concentration the charge capacity of the electrode falls. The pure cobalt oxide electrode is stable but the charge capacity of the electrode is low.

The optical transmittance of several nickel-cobalt oxide electrodes is shown in Figs. 13-15. Optical data for these devices is shown in Table 2. Both the bleached and colored conditions are shown. In Fig. 13. the optical absorption peaks are noted at about 400 and 550 nm with peak transmittance range from $\Delta T_{550}= 0.47$. At 10% cobalt the peak absorption is about 550 nm and the peak transmittance is $\Delta T_{550}= 0.41.5$. In Fig. 14 the optical switching range is lowered further with higher concentrations of cobalt. At 20% cobalt $\Delta T_{550}= 0.28$. and at 40% concentration the is $\Delta T_{550}= 0.18$. The bleached transmittance is still high. As shown in Fig. 15, films made with concentrations above 60% cobalt have a peak transmittance change of less than 10 % .

These result show that pure cobalt electrodes have good transparency in the bleached state but their range of switching is lower when compared to nickel. For concentrations up to 20% cobalt the switching and voltammetry are both good. The increase in oxygen overvoltage is beneficial to the stability of nickel oxide electrodes.

Table 2. Nickel-Cobalt Oxide Electrodes

Electrode	ΔT_{550}	T_p(B-C)	T_s(B-C)
NC39(1%)	47	79-36	54-32
NC40(4%)	43.5	78-37	
NC35(7%)	42.5	74-33	
NC36(10%)	41.5	72-33	
NC120(20%)	28	82-56	
NC122(40%)	18	82-66	
NC123(60%)	10	83-74	54-49
NC124(80%)	7	85-78	
C125	6	85-79	
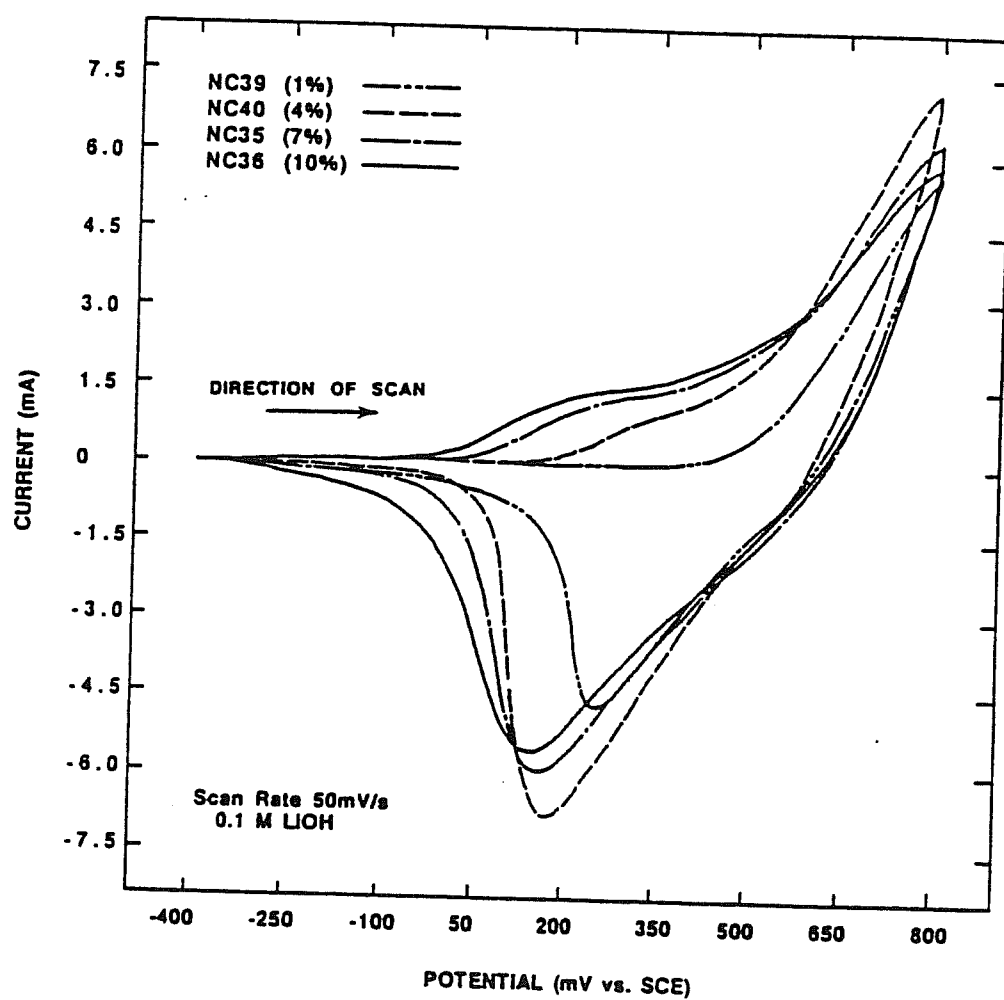
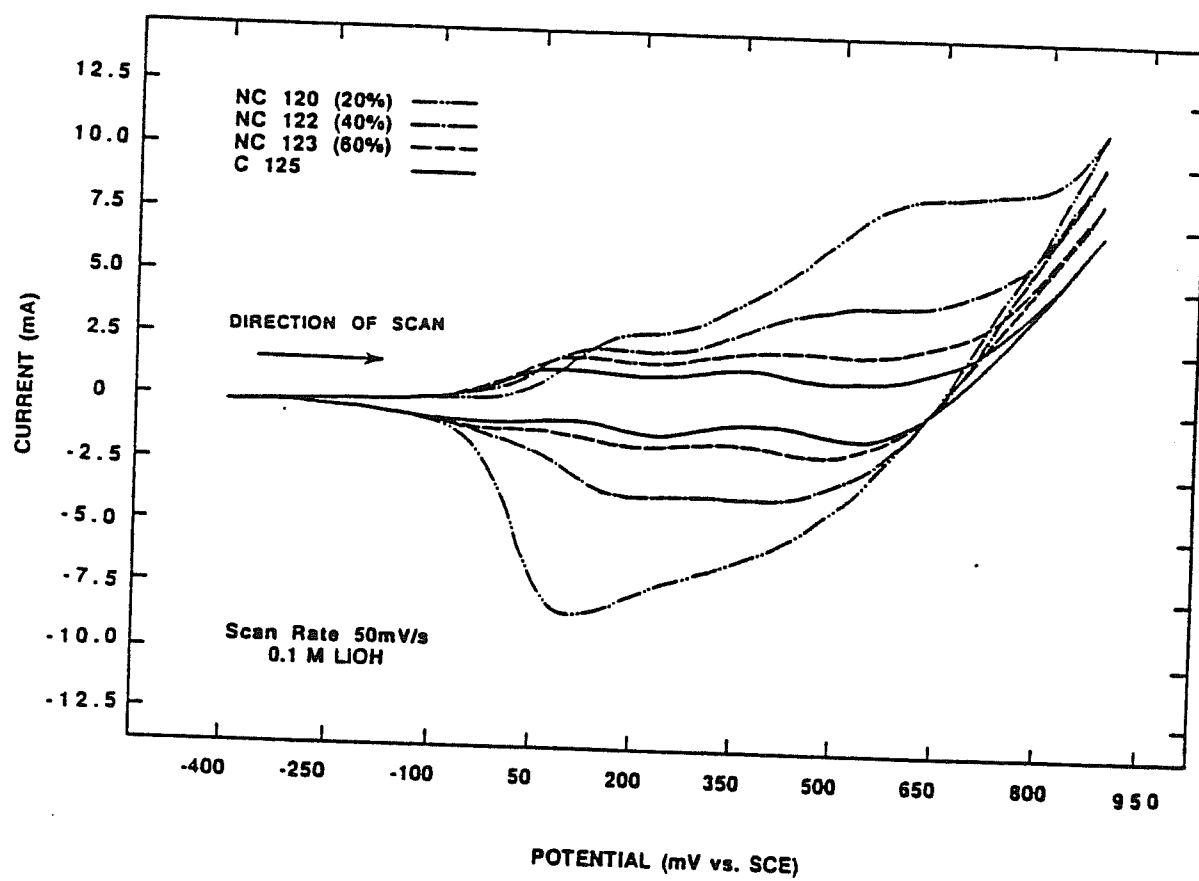Fig. 11. Cyclic voltammetry of electrochromic nickel-cobalt oxide, cycled in 0.1 M LiOH at 50 mV/s.

Fig. 12. Voltammetery of electrochromic nickel-cobalt oxide electrodes. They are cycled in 0.1 M LiOH at 50 mV.
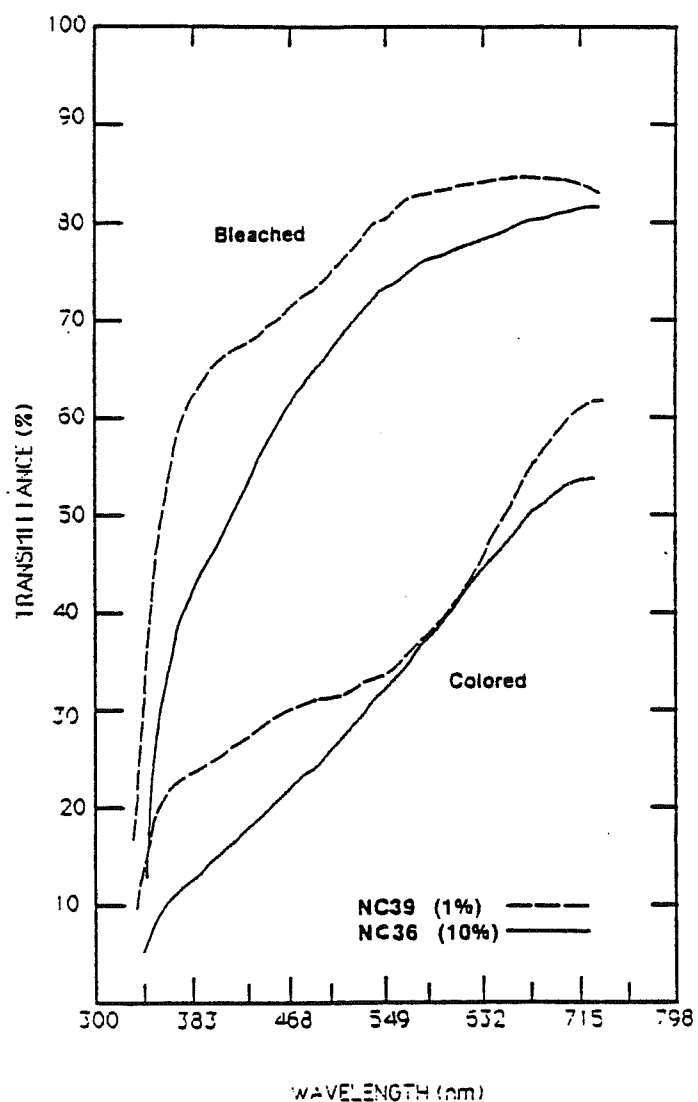
Fig.13. Optical transmittance of electrochromic nickel oxide and nickel-cobalt oxide electrodes. Low concentrations of cobalt are shown
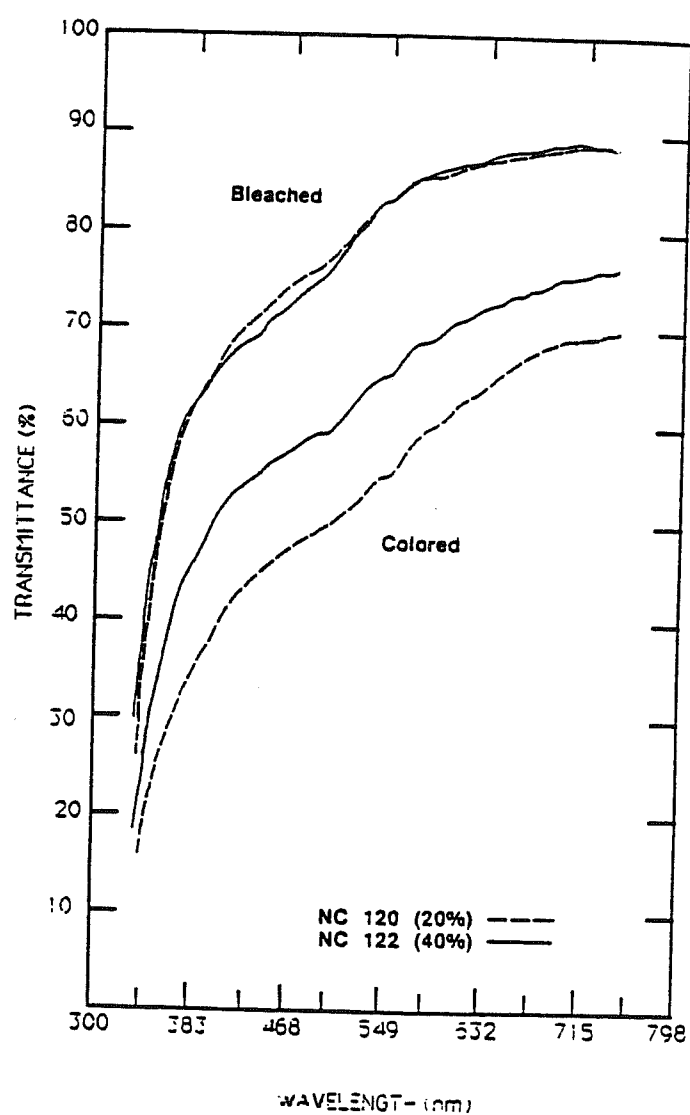
Fig. 14. Optical transmittance of electro-chromic nickel-cobalt oxide electrodes. Medium concentrations of cobalt are shown.
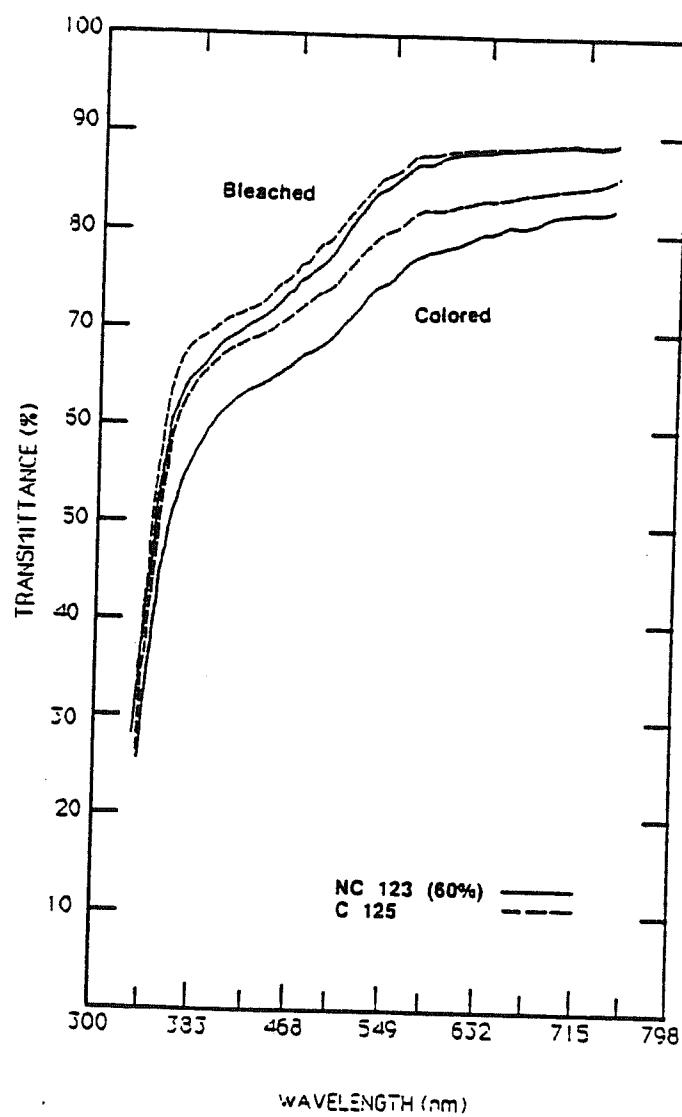
Fig. 15. Optical transmittance of electrochromic nickel-cobalt oxide and cobalt oxide electrodes. High concentrations of cobalt are shown.

4. Tungsten-molybdenum oxide electrodes

Tungsten-molybdenum films were deposited for use as complementary electrochromic electrodes for nickel oxide devices. Tungsten oxide is the most well known electrochromic and it colors from transparent to blue. By doping tungsten oxide with molybdenum oxide the coloration of tungsten can be shifted to grey-blue [21].

Tungsten-molybdenum oxide films were deposited electrochemically [22] from a mixture of solutions of 3 g tungsten metal dissolved in 2% H_2O_2 and 1 g molybdenum metal dissolved in 2% H_2O_2. The molybdenum concentration was adjusted by the ratio of solutions used. The molybdenum concentrations were kept low because molybdenum is favored to deposit over tungsten. Tungsten-molybdenum films were deposited onto ITO electrodes using a triangle potential of -750 to -450 mV (SCE) at 100 mV/s. Most films were made in 50 cycles. After the films were deposited they were rinsed in distilled water, dried with nitrogen and heat treated in an oven at 160 C for one hour.

The voltammetry of the peroxide deposition process is shown in Fig. 16 for a tungsten-molybdenum electrode. Here the data for 10 and 50 scans are shown. Typically, to deposit 100 nm 50 scans are used. During deposition, no characteristic coloring and bleaching are noted. During successive deposition there is an increase in the current, between 10 and 50 cycles the current range increases indicating a d.c. electrode resistivity change from 1.3×10^{-2} to 2.4×10^{-2} ohms.

For voltammetry, and optical transmittance measurements, the electrodes were cycled in 0.1M H_2SO_4 using a calomel electrode and platinum counter-electrode. Cyclic voltammetry for the same film as shown in Fig. 16 is shown in Fig. 17. A voltage range of -1000 to 1000 mV and a scan rate of 50 mV were used. This plot shows the characteristics of a film evaluated at three stages, the characteristic double peak diminishes at long deposition times and after heat treating. In all stages the film colors to grey-blue at negative potentials greater than -0.6V. The sharp negative peak at -1000 mV is part of the hydrogen evolution peak.

The charge-discharge relationship is shown in Fig. 18 for an applied triangle potential from -800 to 800 mV at a scan rate of 25 mV. Here we begin with a highly colored film which quickly bleaches in about 10 s, with a two step current surge followed by no current flow at above 600 mV. On the negative current cycle we note the onset of coloration with its characteristic current surge, again two steps are noted.

Normal transmittance measurements on a tungsten-molybdenum electrode were made over the visible and near-infrared wavelength regions. The electrode was colored using static potentials ranging from 0 to -1.0V with current controlled below 100 mA. The electrolyte was 0.1M H_2SO_4. The typical spectral transmittance (250-1100 nm) of a tungsten-molybdenum oxide electrode in a microcell is reported in Fig. 19. Also, shown in this figure is the transmittance of the empty cell, which only contains the 0.1M H_2SO_4 electrolyte. The switching from 1100 to 2500 nm is about 25% (not shown in the figure). The broad coloration peak centered at 400 nm is characteristic of this mixed oxide [23]. The molybdenum oxide absorption peak is at 1.5 eV and tungsten oxide is at 1.3 eV. Also the increased transmittance at the longer wavelengths is seen in molybdenum and tungsten-molybdenum oxide films [24]. The photopic transmittance of the tungsten-molybdenum oxide electrodes is $T_p = 0.75$ bleached and when colored (-1.0V) switches to $T_p = 0.20$. During cycling we have found these films to be very stable.
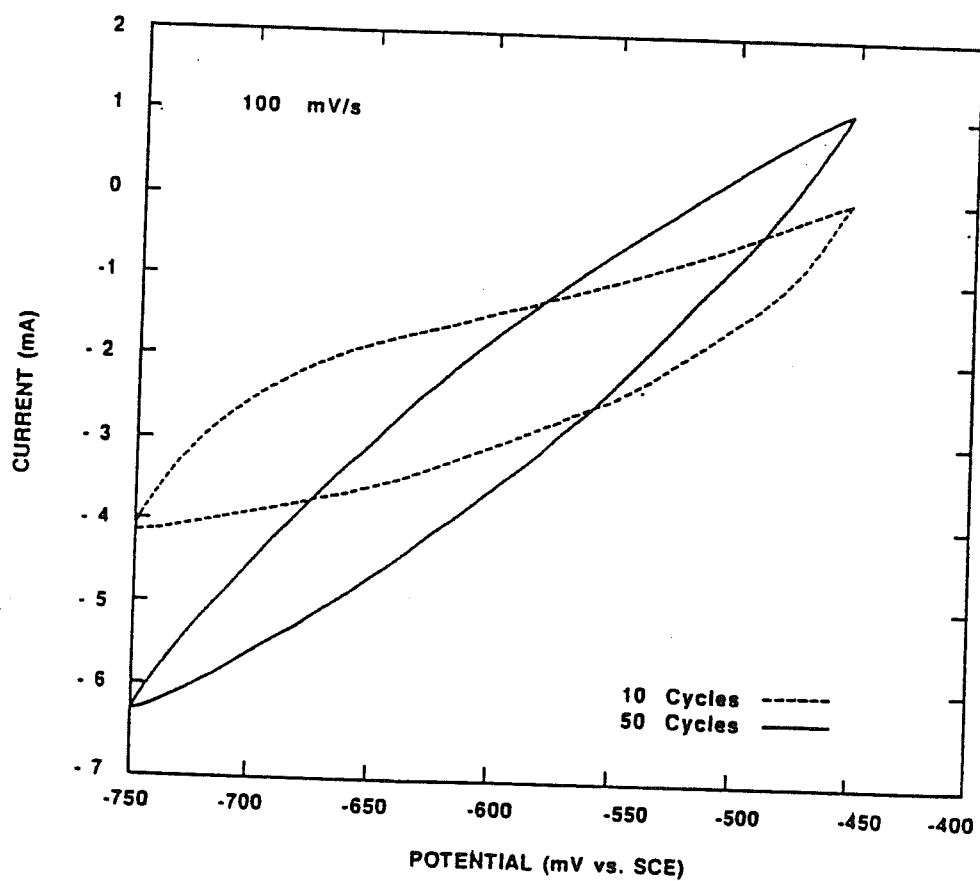
Fig. 16. Voltammetry of the electrochromic tungsten-molybdenum oxide deposition process from a peroxide solution; 10 and 50 scans are shown. The active electrode area is 4 cm^2 .
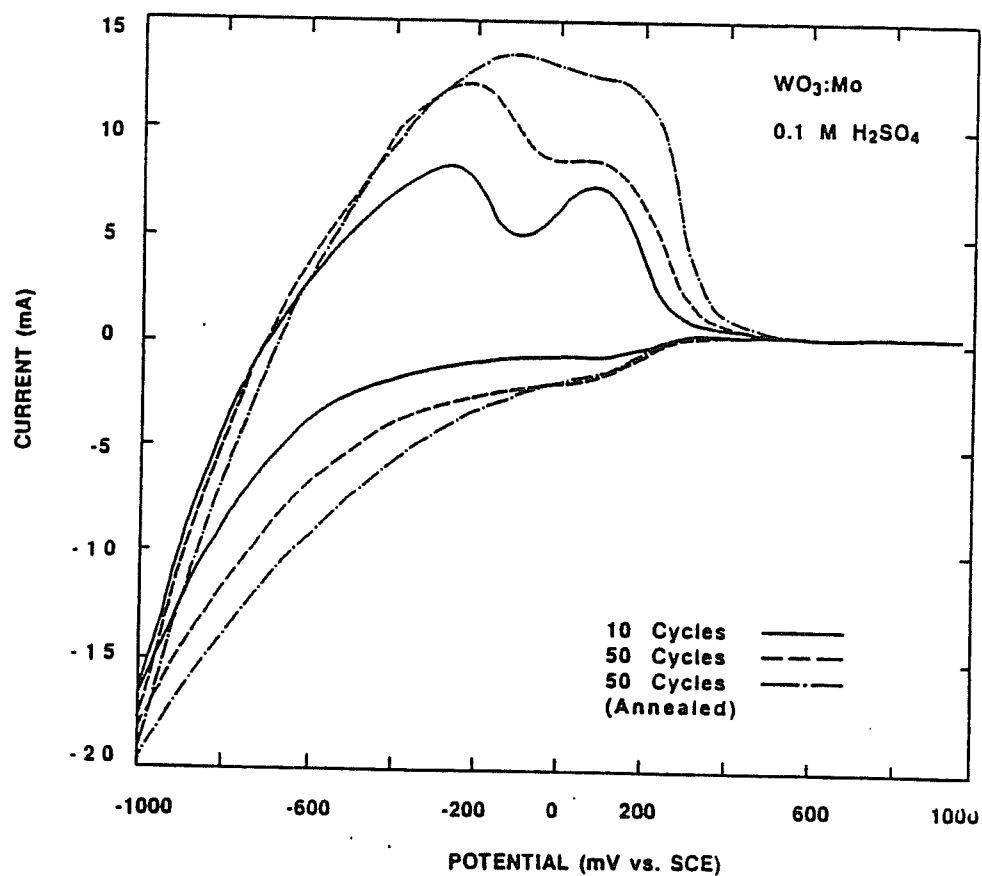
Fig. 17. Voltammetry for a tungsten-molybdenum oxide electrode in 0.1 M H_2SO_4. The scan rate is 50 mV/s. Shown is the response for a film deposited at 10 and 50 cycles and after heat treatment. The active electrode area is 4 cm^2.
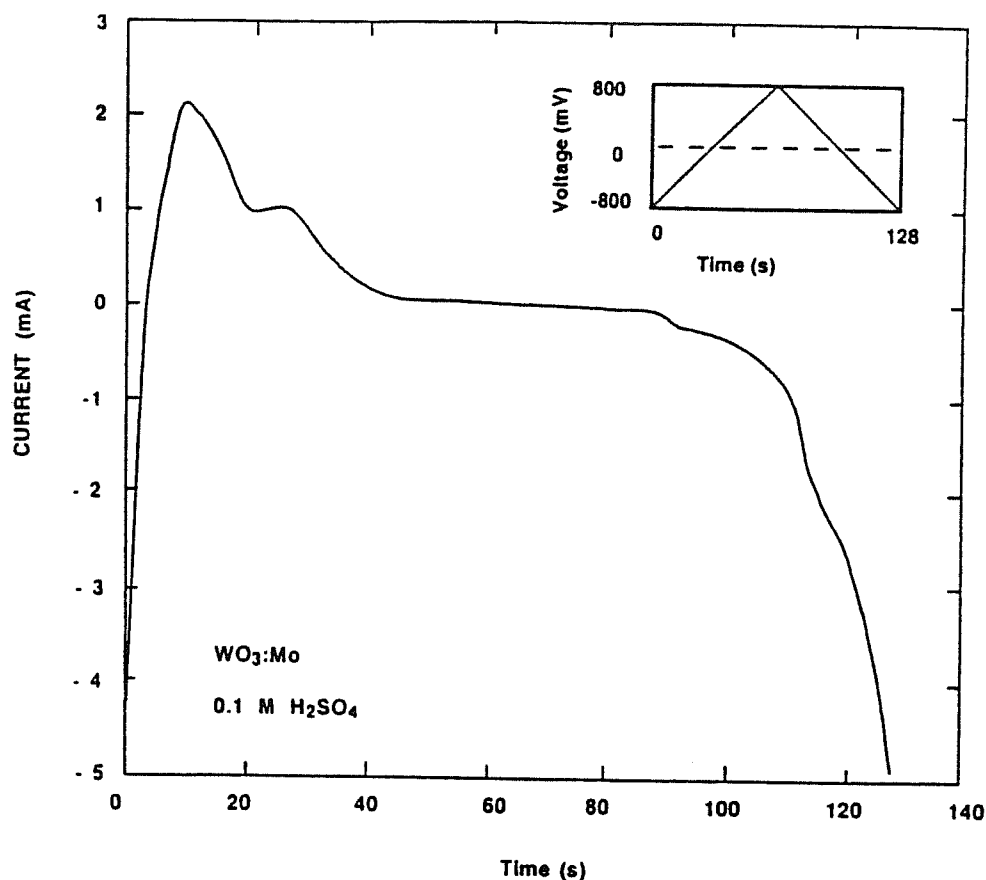
Fig. 18. Charge-discharge relationship for a tungsten-molybdenum oxide electrode in 0.1 M H_2SO_4. The applied potential was a d.c triangle potential, shown in inset. The scan rate is 25 mV/s. The active electrode area is 4 cm^2.
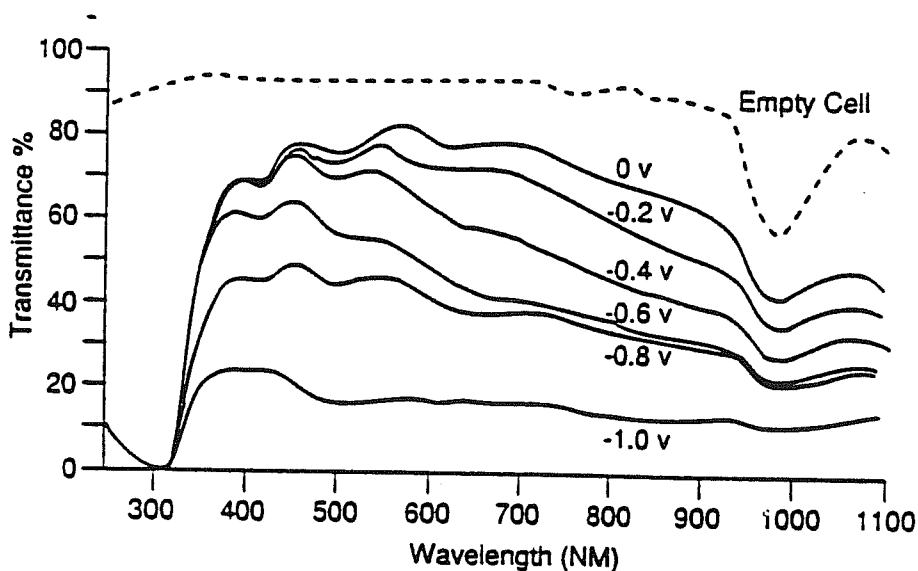

Fig. 19. Normal transmittance for electrochromic nickel oxide in a liquid microcell with 0.1M LiOH electrolyte. Transmittance is shown for different voltages (V vs SCE).

5. Solid polymer electrolytes and Device fabrication

There are two classes of solid polymer electrolytes (SPE) all with ionic conductivities of at least 10^{-6} S/cm. They are polymer-salt complexes and percolation polymers. Polymer-salt complexes exhibit significant conductivity above their glass transition temperature (amorphous state) and these are generally complexes of polyethers and alkali metal salts. They are ion solvating. For the polymer salt complexes, conduction is achieved by a cooperative interaction between the mobile ionic species and the amorphous polymer matrix. These polymers generally conduct both by anionic and cationic conduction. For these polymers the conductivity first increases with increased conductive phase but reaches a maximum because the glass transition temperature is increased, resulting in restricted polymer segment motion and deceased ionic conductivity. Percolation polymers are polymers which have ionic conductivity below the glass transition temperature; examples are Nafion, polyalcohol-acid complexes. They conduct by percolation in which a highly conductive phase is embedded in a poor conductor. This type requires a critical volume of the conductive phase to be conductive. The material undergoes an insulator to conductor transition when the percolation threshold is exceeded, after which there is no further change in conductivity with higher volume fractions of the conductive phase.

The polymers used to make polymer ion conductors for devices we based on amorphous poly(ethylene oxide)- a-PEO, related copolymers of a-PEO, and poly(ethyleneimine)-PEI, $[CH_2-CH_2-NH]_n$. These polymers were chosen for a variety of reasons. First they have been very successful in the development of polymeric batteries and a-PEO has one of the highest ionic conductivities known for a polymer [25]. Second, they are fairly simple linear polymers, with reasonable solubilities to a variety of solvents and salts. Third, they are highly transparent (greater than 95% in the visible region) and can be formed into free standing films or be used for solution and spin coating. They are highly elastic and adhesive so they can serve as a laminating polymer for devices. Finally they are low cost, non-toxic in their final form. These polymers are used as system to develop polymer ion conductors, other polymers have potential for use to including poly(vinylbutral) used in safety glass as the protective inner laminate and poly(methyl methacralate) and related copolymers.

PEO is one of many polyoxides; it is composed of $[CH_2-CH_2-O]_n$. Because PEO normally will crystallize at room temperature, forming spherulites, the amorphous form is used. Also, the amorphous form has the highest ionic conductivity . In general, this group of polymers has about 10^{-4} S/cm (25 C). with about 10^{-13} S/cm d.c. electrical conductivity (25 C). The dielectric breakdown of a typical 50 um thick Li- PEO film is about 3×10^5 V/cm For reference the conductivity of 1M KOH is 1.6×10^{-1} S cm^{-1}. Various types of solid polymer electrolytes (SPE) can be made. For all PEO based polymers the amorphous to crystalline phase transformation must be suppressed. This is done by the introduction of a compound that will react with the polymer and cause chain termination. Some of the typical compounds are ones containing ClO_4^-, $CF_3SO_3^-$. To make a lithium ion conduction we have used $LiCF_3SO_3$ and related triflates, for sodium ion conduction $NaCF_3SO_3$ mixed with solvating aprotic polymer . The salts concentration in the polymer are usually expressed as the ratio of oxygen atoms (corresponding to the monomer , ethylene oxide (EO)unit) to the metal ion or O/M ratio. In all formulation there must be acid-base stability of the complex formed between solvating EO chains and a metal salt. The Lewis acid-base equilibrium is necessary for stability and complex formation following $M^+AX_n^- + x(EO) \longrightarrow M^+(EO)_xAX_n^-$ and AX_n^- anions should not be involved in a Lewis acid-base equilibrium, such as $M^+AX_n^- + (EO) \longrightarrow (EO)_xAX_{n-1}^- + MX$. Also it is important that no other chemical reactions occur with the solvent. PEO has electrochemical stability to oxidation especially at fairly high voltage levels >4.6V. There should be stability at the electrode/SPE interfaces. Li-PEO-CF_3SO_3 complexes have been tested at 100 - 170 C with good stability [26], at 170 C the redox stability domain drops below 2 V. The Li-

PEO-CF$_3$SO$_3$ polymer complex generally conducts both cation and anion species, and are defined by transport numbers [27]. Typical transport numbers (90 C) for PEO--LiI and PEO-LiClO$_4$ are t$^+$ =0.3, t$^-$=0.7 and PEO-LiCF$_3$SO$_3$ t$^+$=0.7 and t$^-$=0.3.

Three polymer electrolytes were prepared in this study. Two were prepared from PEO, the third from PEI. The PEO electrolytes were prepared from a base of 5 million molecular weight PEO with acetonitrile as a solvent. Solutions of about 2-4% PEO to solvent were made. To this was added a salt, such as lithium triflate (LiCF$_3$SO$_3$) of the ratio 20 EO/1unit salt. This solution was stirred slowly for 2-4 days with a magnetic stirrer to a uniform gel consistency. We have used other solvents such as chloroform (dissolves up to 30 wt % PEO), water+methanol (up to 10% PEO), water (up to 30% PEO),dichloromethane (up to 10% PEO), ethanol (up to 30 % PEO), acetone (up to 8% PEO), and dimethylformamide (up to 30% PEO). Care must be taken to not precipitate the polymer or salt out of solution. It was possible to color tungsten-molybdenum oxide electrodes using PEO-lithium triflate. Other compounds were added to enhance anion or hydroxyl conduction. Additional additives that colored nickel oxide and nickel-manganese oxide were sodium trimethylsilanolate, (CH$_3$)$_3$SiONa, sodium tetraborate Na$_2$B$_4$O$_7$, sodium metasilicate, Na$_2$Si$_3$O$_7$. These oxides were added in amounts ranging from 1-10% depending upon solubility and optical properties. In general, the addition of soluble salts and oxides did not greatly alter the optical properties of the PEO film. A 5um thick film of PEO has about 95% transmission from 300 to 1100 nm. Another polymer was formulated using PEI, a molecular weight of approximately 60,000 was used. This polymer could not be used with tungsten-molybdenum electrodes since it etched the film.

These polymers can be coated on electrodes using, solution casting, doctor blades, dipping or spin coating or reverse roll coating. The PEO-polymers can be cast into free standing films by the use of glass casting rings. Free standing films of 10 um and greater have been made. These films are very adhesive and must be cast on teflon. High solvent concentrations are used with PEO because of its elastic properties, making it hard to work with at lower solvent concentrations. It can have a consistency similar to silicone adhesive. The technique used depends upon the rheological properties of the specific SPE. The SPE is very versatile, it can be easily modified according to the intended electrochromic device application, its specific ion or ions need for coloration and its charge storage needs.

The electrochromic device structure is shown in Fig. 20. It was constructed from two coated electrodes. Lamination is performed in air after drying of the SPE layer. The edges of the device were sealed with UV curable polyimide optical adhesive. Other sealants can be used such as silicone and polyurethane. Care must be taken to insure that the sealant and its curing byproducts do not react with or interfere with the SPE or electrochromic layers. Reference electrodes were not used in these fabrications.

Completed 3 x 3 devices were tested using a d.c power supply with current regulation. All voltage are relative to the nickel oxide electrode. The devices were optically evaluated using a spectrophotometer. The spectra of the devices are shown in Figs. 21-24. Optical data on all devices is in Table 3. The device in Fig. 21 is of the complementary design using an anodically (nickel oxide) and cathodically (tungsten-molybdenum oxide) coloring electrochromics. In this design both electrochromics color together to a grey-bronze. Both electrodes color but not a strongly as they do independently of each other. Also, the potentials are higher than the other devices, many devices will begin to switch at 1.4-1.8 V. In the device in Fig. 21 the SPE electrolyte is a-PEO with lithium triflate and sodium silanolate. The sodium sianolate is an organic equivalent to sodium hydroxide. After switching for several cycles and holding for prolonged times at 2.7V small bubbles formed in the device, probably from residual solvent. With some refinement of the SPE layer this device holds promise, being one of the few electrolytes that both colors tungsten and nickel oxides without appreciable etching of the tungsten layer during film casting. This device switched from

T_p(bleached)= 0.79 to T_p(colored)=0.39. The corresponding solar transmittance was T_s(bleached)=0.55, T_s(colored)=0.35. (data not shown in figure).

The device in Fig. 22 is a nickel oxide/nickel oxide-manganese oxide device. The nickel-manganese layer was made with a 60% manganese sulfate solution. The SPE is a-PEO with lithium triflate and sodium metasilicate. This device colored well above 1.4 to 2.0V, but became partly irreversibly colored above 2.4V, during saturation testing. Disassembly of the device may reveal what caused the permanent coloration of the device. This device also holds promise, the SPE is one of the best made thus far. This device compared to the complementary device (in Fig. 21) shows deeper coloration but with a narrower bandwidth (mainly visible) while the complementary device shows greater bandwidth including the near infrared. This device switched from T_p(bleached)=0.71and T_p(colored)=0.23. The corresponding integrated solar transmittance was T_s(bleached)=0.52, T_s(colored)=0.44 (data not shown in figure).

The device in Fig. 23 is another nickel oxide/nickel oxide-manganese oxide device. It was made with poly(ethyleneimine), PEI (containing some water) and sodium tetraborate. This SPE has the consistency of a viscous grease and never dries to a hard film. It colors nickel very well, but may also etch it over long periods of time. PEI can not be used with tungsten oxide, as it very effectively removes the coating. This device colors strongly at 2.1V. Small bubbles formed at 2.5V, probably from the residual water in the SPE. This electrolyte holds less promise than the a-PEO types, but it is easy to fabricate devices from. It is worthwhile to investigate making PEI films from the dry polymer.

The device in Fig 24 is another nickel oxide/nickel oxide-manganese oxide device. It is made without an SPE, but rather with an inorganic sodium borate-silicate glassy mixture. This device colored only 10% at 1.2V and its switching was slow. Higher voltages did not give higher coloration. Spot tests did show deeper coloration for nickel oxide. This coating was about 5 um thick and it is expected that a thinner film of this glass may give improved performance. A sol-gel deposited form of this glass may be very effective.

Table 3. Nickel-Oxide Devices

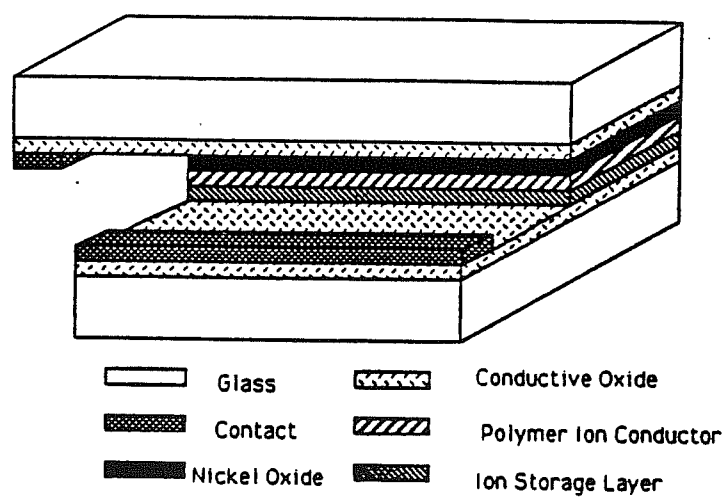| Device	Peak λ,nm	ΔT_{peak}	T_p(B-C)	T_s(B-C)
NiO/PEO+Sianolate/WO$_3$	560	43	79-39	55-35
NiO/PEO+Silicate/NiO:Mn	550	44	71-23	52-44
NiO/PEI+Borate/NiO:Mn	460	48.5	54-22	45-34
NiO/Borate+Silicate/NiO:Mn	460	10.5	62-53	48-42

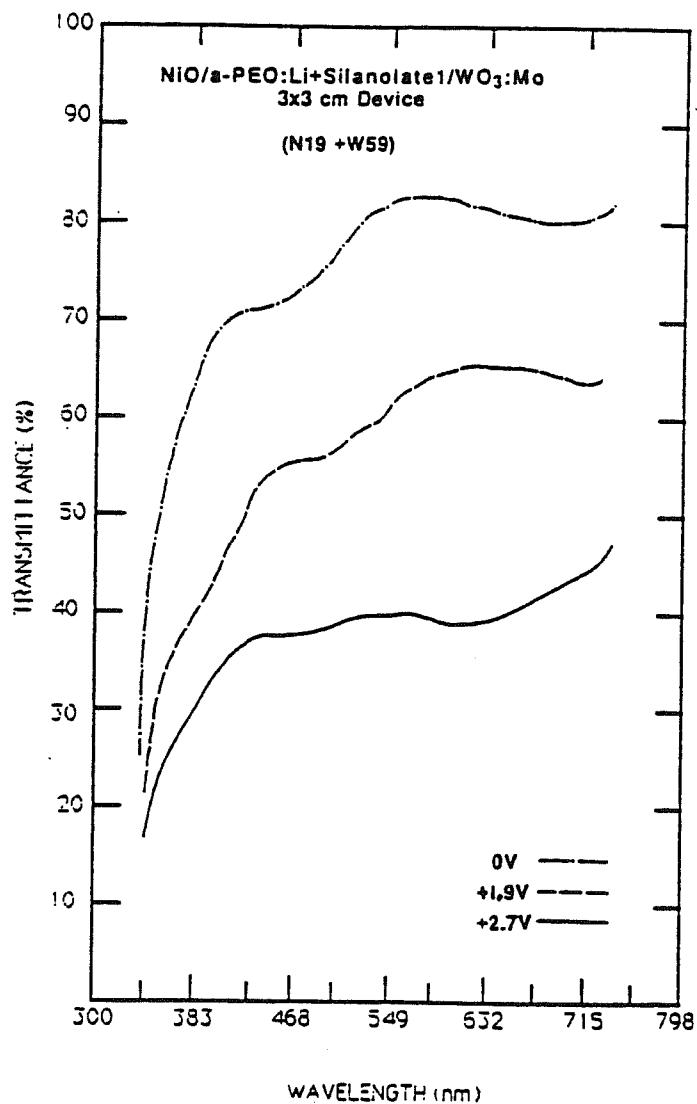Fig. 20. Schematic construction of 3 x 3 cm electromic devices, showing the various layers. (not to scale)

Fig.21. Optical transmittance of electrochromic nickel oxide/a-PEO/ tungsten-molybdenum oxide The device potential was 1.9V and 2.9V.
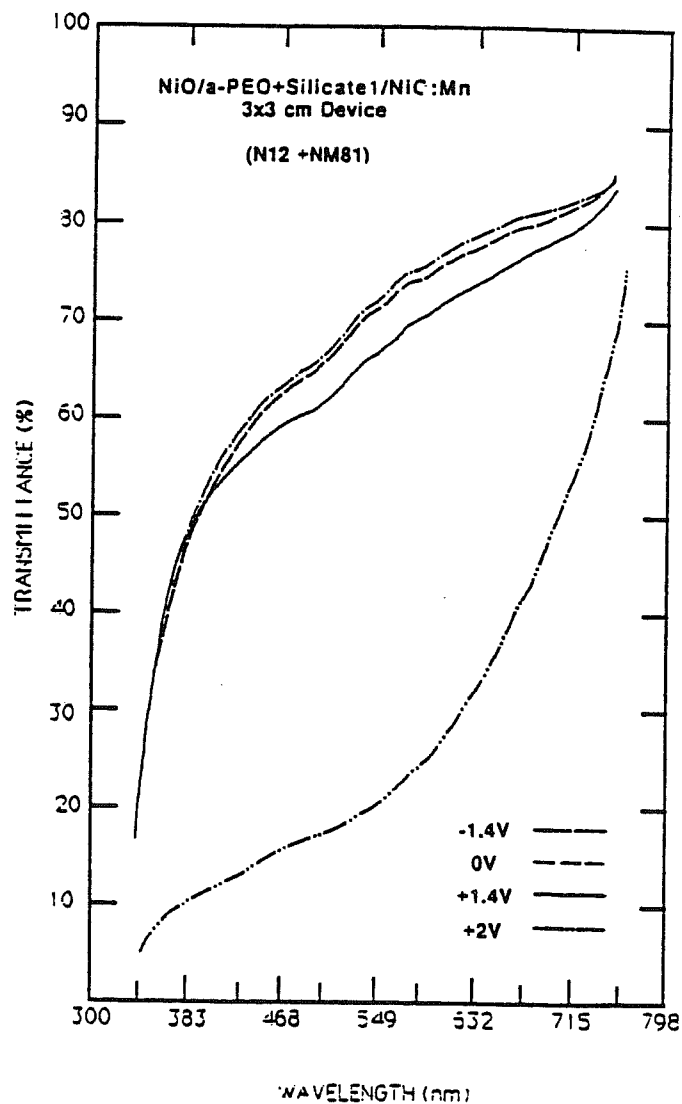

Fig. 22. Optical transmittance of electro-chromic nickel oxide/a-PEO/nickel-manganese device. The applied potential was 1.4V and 2V and -1.4V.
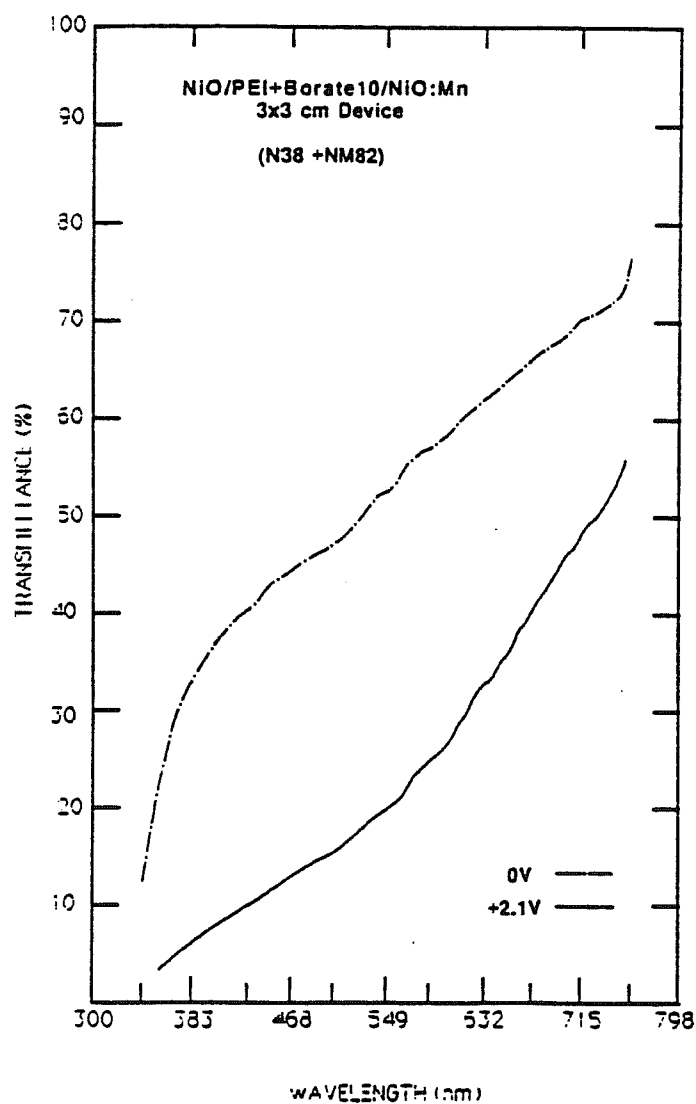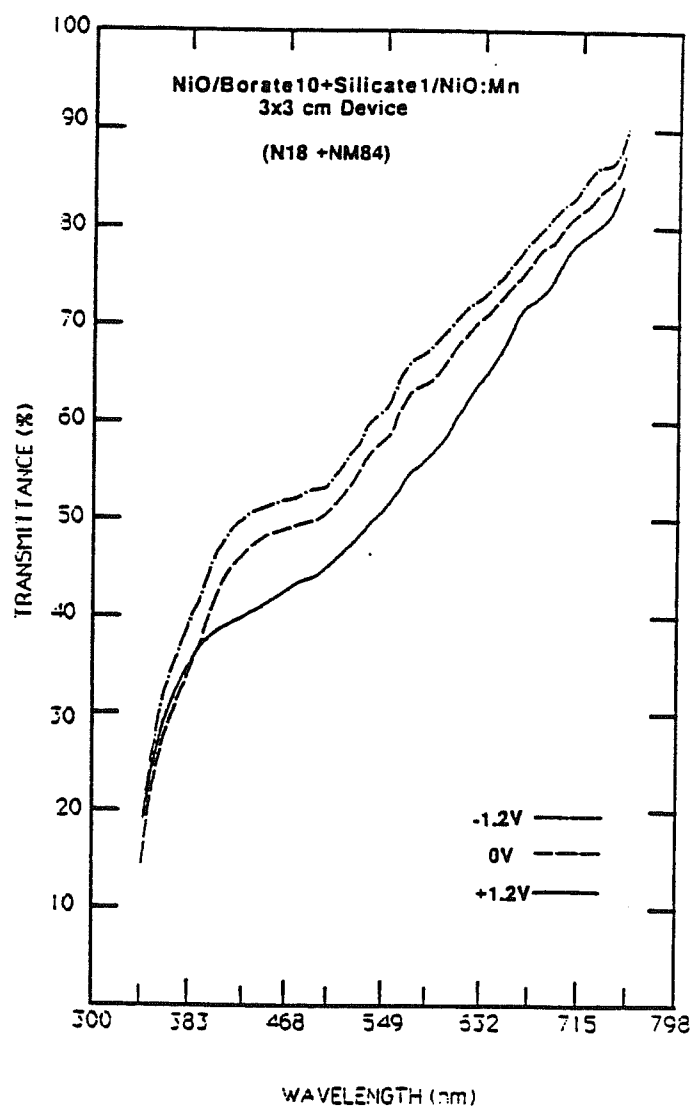
Fig.23. Optical transmittance of electrochromic nickel oxide/a-PEI/ nickel-manganese oxide The device potential was 2.1V.

Fig. 24. Optical transmittance of electro-chromic nickel oxide/borate-silicate/nickel-manganese device. The applied potential was 1.2V and -1.2V.

Conclusions and Recommendations

Our work on electrodes has shown that very excellent electrochromic electrodes can be made. By the addition of manganese to nickel oxide the coloration and electrical properties can be altered. At low manganese concentrations the films behave similar to nickel oxide films, with increased oxygen overvoltage. At manganese additions above 50% the electrodes decrease their switching but retain their charge storage characteristics. Thee are used for counter-electrodes for nickel oxide devices. Pure manganese oxide could not be stabilized to be useful. The addition of cobalt to nickel oxide was investigated. Small amounts of cobalt slightly increase the switching range of nickel oxide while increasing the oxygen overvoltage. Higher cobalt concentrations give decreased optical switching, and may have use as counter-electrodes. Pure cobalt films do not switch and show a flat voltammetry. High quality tungsten-molybdenum oxide films have been successfully deposited from peroxide solution. The addition of molybdenum alters the blue coloration of tungsten oxide to a grey-blue.

The work on solid polymer electrolytes for electrochromic devices is developing. The best solid polymer electrolytes were a-PEO (triflate based) containing sodium silanolate, silicate or borate. Some of these polymer could be used for complementary device using tungsten/ nickel oxide devices. Further refinements in synthesis and improvements in fabrication are required to make SPE based devices more durable. The use of an inorganic ion conductive borate-silicate glass appears interesting. Techniques to make thinner film may offer promise. With all the advances being made in the polymer battery field, it is expected that a wide range of polymers will be available. A new form of truly amorphous PEO copolymer known as oxymethylene linked poly(oxethylene) oxide, with reported conductivities 1-2 orders of magnitude lower than the PEO-triflate has been synthesized. Our future devices will be fabricated using this new polymer.

Our best nickel oxide/aPEO/tungsten-molybdenum device showed the photopic transmittance (T_p) to be T_p(bleached)=0.79 and T_p(colored)=0.39. The corresponding integrated solar transmittance was (T_s) to be T_s(bleached)=0.55, T_s(colored)=0.35 . Our best nickel oxide/a-PEO/nickel-manganese device showed the photopic transmittance to be T_p(bleached)=0.71and T_p(colored)=0.23. The corresponding integrated solar transmittance was T_s(bleached)=0.52, T_s(colored)=0.44

Acknowledgements

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